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Exchanges of Carbon in the Coastal Seas

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In the natural carbon cycle, the time period for atmosphere-biosphere exchange ranges from only a few months to a few decades. The exchange of CO_2 between the atmosphere and the hydrosphere, by contrast, takes several hundred years if the interior of the oceans is taken into consideration. The exchange is much more rapid, however, on a time scale of a few years or even less, for only the terrestrial hydrosphere and the surface mixed layer of the oceans. The time for the atmosphere-lithosphere exchange is very long, requiring many thousands of years or more. The shallow sediments on the continental shelves interact relatively readily with the atmosphere. Some terrestrial material even crosses the shelves, which have a mean width of 70 kilometers (km) and a total area of 26×10^6 km^2, and efficiently reaches the slopes, which start at an average depth of 130 meters (m) (Gattuso et al. 1998). Dissolved organic matter may also be swiftly carried to the interior of the oceans through intermediate bodies of water in certain areas, including the Arctic, Okhotsk, Mediterranean, and Red Seas (Walsh 1995; Chen et al. 2003). The specific rates of productivity, biogeochemical cycling, and sequestration of CO_2 are higher in the continental margins than in the open oceans. The end result is that it may take only years, as opposed to hundreds of years, for the atmosphere, lithosphere, biosphere, and hydrosphere to interact in the continental margins. These zones may also act as major conveyor belts, transporting carbon to the interior of the oceans.

In general, the coastal oceans tend to absorb CO_2 in winter, when the water cools, and in spring, as a consequence of biological processes. In summer and fall, the processes of warming, respiration of marine organisms, and decomposition of organic matter release CO_2 back into the atmosphere. Bacterial processes involved in the production of CH_4 (methanogenesis) as well as in the biological production of dimethyl sulfide (DMS) on the shelves also release these important greenhouse or reactive gases into the atmosphere. Finally, direct and indirect human perturbations to the continental margins (e.g., pollution, eutrophication) are large and have dire consequences for marine ecosystems. Unfortunately, owing to the diversity and therefore complexity of the shelf systems, their precise roles in the carbon cycle have yet to be quantified with any degree of certainty. There is still, in fact, no consensus on the simple question posed by the Land-Ocean Interaction in the Coastal Zone project (LOICZ) in its first report: Are continental shelves carbon sources or sinks? (Kempe 1995).

Basing their argument on the imbalance between the total river transport of about 0.4 petagrams of carbon per year (PgC y^{-1}) and the oceanic organic carbon burial rate of around 0.14 PgC y^{-1}, Smith and Mackenzie (1987) and Smith and Hollibaugh (1993) noted that the ocean must be heterotrophic, releasing more CO_2 into the atmosphere than it takes up, in the absence of the anthropogenic perturbation of atmospheric CO_2. Over the long term, the difference of 0.26 PgC y^{-1} is most likely returned to the atmosphere. Ver et al. (1999a,b) and Mackenzie et al. (2000) evaluated changes in the carbon cycle of the continental margins over the past three centuries. These three studies conclude that continental margin waters are still a source of CO_2 to the atmosphere in spite of increased invasion of CO_2 from the atmosphere to the continental margins driven by the rise in atmospheric CO_2. Fasham et al. (2001) adopts the same view and reports a net sea-to-air flux of 0.5 PgC y^{-1} for continental margins.

The Mass Balances

The most recent Joint Global Ocean Flux Study (JGOFS) synthesis, however, suggests that the marginal seas are sinks of CO_2 (Chen et al. 2003). This synthesis, with slight modifications to reflect some recent developments, indicates that the global average new production of phytoplankton on the shelf is 0.78 Pg y^{-1} particulate organic carbon (POC) and 0.25 Pg y^{-1} particulate inorganic carbon (PIC) (Figure 18.1, Table 18.1). This new production is only 13 percent of the average primary production rate and is mostly a result of upwelling (Chavez and Toggweiler 1995; Liu et al. 2000; Chen 2000, 2003a). Although net community productivity is rather high on global shelves (Lee 2001), only about 0.2 PgC y^{-1} of PIC and the same amount of POC out of the total production (0.48 Pg y^{-1} PIC and 6.2 Pg y^{-1} POC) is buried and stored on the shelf. Downslope transport of modern particulate carbon is 0.5 PgC y^{-1}, 58 percent of which is organic (Chen et al. 2003). Results from major programs on the eastern United States, western European, East China Sea, and Mediterranean continental shelves all show that most of the biogenic particulate matter is remineralized over the shelves. Only a small proportion (<8 percent) is exported to the adjacent slopes (Wollast and Chou 2001; de Haas et al. 2002; Chen 2003b), but higher export ratios have occasionally been reported.

The downslope transport of POC is only 23 percent of the offshore transport of dissolved organic carbon (DOC). Recent studies based on ^{13}C, ^{14}C, and ^{15}N show that a large portion of the off-shelf transport of POC may be old terrestrial or relic matter.

Table 18.1. Fluxes relevant to continental margins.

Category	*Values*
Rivers plus groundwater and ice	• DIC: 32 (1, 6) • DOC: 30 (1), 27 (6) • PIC: 15 (1, 6) • POC: 20 (1), 18 (6) • IC: 37 (7), 13 (9) • OC: 34 (2), 30 (7), 31 (8)
Air-to-sea (gaseous)	• CO_2: 25 (1), 20 (2), 49 (3), 46–75 (4), 30 (6), 8.3 (7), 62 (10), 83 (11); • CH_4: -0.1 (6); • DMS: -0.07 (6)
Precipitation plus dust	• PIC: 0.3 (1, 6); OC: 0.2 (8)
Net burial plus fish catch	• PIC: 15 (1, 6, 9), 14.5 (9); POC: 15 (1, 6, 9), 14 (2) • Total: 12.5 (7)
Gross upwelling plus surface inflow	• DIC: 2800 (1), 2827 (6); • DOC: 80 (1), 70 (6); • POC: 4 (1, 6)
Downslope export of particulates	• PIC: 20 (1, 6, 9); • POC: 20 (1, 9), 27 (6); • Total: 167 (7)
Gross surface water outflow	• DIC: 2800 (1,6); • DOC: 120 (1, 6); • PIC: 1.0 (1, 6); • POC: 12 (1), 22 (6); • Net: 58 (7)
Gross offshelf export (downslope + surface outflow)	• DIC: 2800 (1, 6); • DOC 120 (1, 6); • PIC: 21 (1, 6); • POC 32 (1), 49 (6); • Net: 225 (7)
Net offshore export (downslope + surface outflow-upwelling plus surface inflow)	• DIC: 0 (1), -27 (6); • DOC: 40 (1), 50 (6), 33 (13); • PIC: 21 (1, 6); • POC: 28 (1), 45 (6); • IC 4 (9); • OC: 40 (2), 38 (12); • Total: 58 (7)

(continued)

Table 18.1. *(continued)*

Category	*Values*
Primary productivity	• PIC: 40 (1, 6, 9), 24.5 (9);
	• POC: 516 (1, 6,9);
	• OC: 368 (2), 789 (5);
	• Total: 830 (7)
New productivity	• DOC: 23 (6);
	• PIC: 6 (1), 21 (6);
	• POC: 75 (1), 42 (6);
	• OC: 43 (2), 231 (5), 158 (13),
	• Total: 167 (7)
f-ratio	• 0.15 (1), 0.12 (2), 0.29 (5), 0.2 (7), 0.13 (6)

Note: All values except f-ratio are in 10^{12} moles C y^{-1}; numbers in parentheses are reference numbers. Traditionally these values are given in moles C and are not converted to PgC.
Sources: 1. Figure 17 and Table 8 of Chen et al. (2003) and the 27 references therein; 2. Rabouille et al. (2001); 3. Yool and Fasham (2001); 4. extrapolated from data on the European shelves by Frankignoulle and Borges (2001); 5. Gattuso et al. (1998); 6. this study; 7. Liu et al. (2000); 8. Smith et al. (2001); 9. Milliman (1993) and Wollast (1994); 10. Walsh and Dieterle (1994); 11. Tsunogai et al. (1999); 12. Alvarez-Salgado et al. (2001a) and 13. Hansell and Carlson (1998).

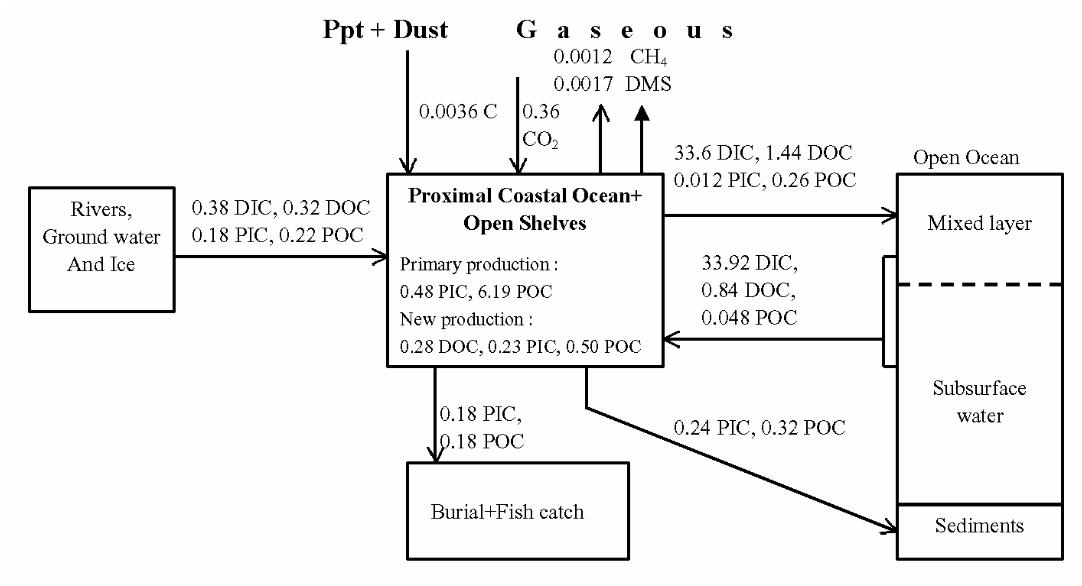

Figure 18.1. Schematic diagram for the annual carbon budget (in 1012 mol PgC y-1) for the continental margins of the world (modified from Chen et al. 2003).

There have been reports of high PIC contents on the slopes (Chen 2002; Epping et al. 2002), but whether or not these are relic is unknown (Bauer et al. 2001). Net off-shelf transport of DOC is 0.60 PgC y^{-1}, about twice terrestrial input of 0.32 PgC y^{-1} (Figure 18.1). The remaining 0.28 Pg y^{-1} DOC is produced on the shelves and represents 35 percent of new organic carbon production, or 27 percent of total new carbon production, a finding that is consistent with the results of Hansell and Carlson (1998).

Marginal seas are also sources of CH_4 and DMS (Sharma et al. 1999; Marty et al. 2001). For CH_4, shelf sediments are likely to be the principal source, whereas for DMS, biological production in the water column is probably the main source. These fluxes are small (Figure 18.1) compared with the very large CO_2 fluxes, but they play an important role, based on their activity in absorbing solar energy and reactivity in the atmosphere.

The pCO_2 of the Continental Margins

The discussion so far deals with carbon balances rather than the CO_2 partial pressure (pCO_2) of surface waters. Yet, for surface waters to be a source or sink for atmospheric CO_2, their pCO_2 must respectively be larger or smaller than atmospheric pCO_2. Estuaries are generally supersaturated with CO_2 largely as a result of the respiration of organic carbon input from rivers (Frankignoulle et al. 1998; Abril et al. 2002). The shelf systems have not been studied as thoroughly. The first comprehensive study of pCO_2 on a large shelf was conducted in the North Sea in May and June 1986 (Kempe and Pegler 1991). According to that study, the North Sea gained 1.4 mol C m^{-2} y^{-1}. Since that study, many more pCO_2 data have become available. Frankignoulle and Borges (2001), for instance, measured pCO_2 during 18 cruises in the surface waters of many northwest European shelves. Their results show that these shelves are a sink of 0.09–0.17 PgC per year. This is an additional, appreciable fraction (45 percent) of the proposed flux for the open North Atlantic Ocean (Keir et al. 2001; Takahashi et al. 2002).

Data on surface water pCO_2, temperature, and salinity have been collected over all four seasons in the Yellow Sea and the East China Sea (ECS). These seas are a year-round CO_2 sink (Chen and Wang 1999; Tsunogai et al. 1999). Low pCO_2 has also been reported for the Bering and Mediterranean Seas, along the Californian coast, the Bay of Bengal, and many other locations (see tables compiled in Chen et al. 2003 and Chen 2003b). Gattuso et al. (1998) compiled all of the available data for coastal ecosystems and concluded that the proximal shelf regions that are directly influenced by the input of terrestrial organic matter are net heterotrophic. That is, they release CO_2 into the atmosphere because respiration is greater than biological production. The distal shelves are net autotrophic, owing to the smaller influence of terrestrial inputs and to the larger export of carbon to sediments and across the continental shelf break. The results compiled by Chen et al. (2003) and Chen (2003b) confirm the findings of Gattuso et al. (1998) and show that the global shelves are CO_2 sinks.

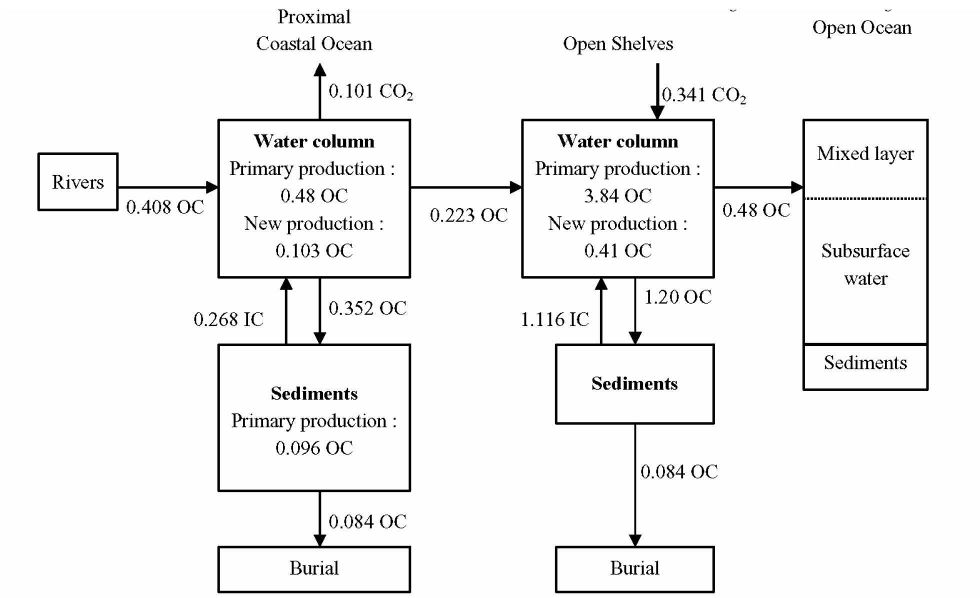

Figure 18.2. Organic carbon cycle in global coastal oceans in its preanthropogenic state. The boxes represent the reservoirs, and the arrows represent the fluxes between them. The air-sea fluxes do not include the net flux of CO_2 because the carbonate system is not included in the budget (data taken from Rabouille et al. 2001).

The temporal link between high winds and low sea-surface pCO_2 leads to a situation in which average sea surface pCO_2 can be supersaturated, and the net annual flux is still from the atmosphere to the sea. This situation occurs because the highest fluxes generally occur in winter and spring, during periods of undersaturation when the winds are strong. Exchange rates are lower in summer and fall when surface waters are generally more supersaturated and the winds are weaker (Memery et al. 2002). Many studies assume that an autotrophic system absorbs CO_2 from the atmosphere (e.g., Smith and Hollibaugh 1993), but intensive upwelling regions may be autotrophic and still release CO_2 to the atmosphere. This process can happen when the pCO_2 of shelf waters is reduced as a consequence of a decrease in the ratio of total CO_2: alkalinity due to dissolution of relic carbonate deposits and/or increased alkalinity due to sulfate reduction in the sediments (Chen 2002). In a recent study of the East China Sea continental shelf, Tsunogai et al. (1999) suggested that because the shallow seafloor restricts the convection of cooling water, cooling is greater for waters on the continental shelf than for waters in neighboring open oceans. This process leads to a "continental shelf pump," driven by the production of relatively cold and dense water, which, in combination with biological production, increases the absorption of CO_2 in the continental shelf zone. Based on a globally distributed sample of 33 shelves and marginal seas, Yool and Fashman (2001) found that the continental shelf pump accounts for a net oceanic uptake of 0.6 PgC y^{-1}. For the situation prior to human effects, Mackenzie and colleagues concluded that, "Before anthropogenic activities, the global coastal ocean was a net autotrophic system with a net export flux to sediments and the open ocean of 20 T mol organic C/yr (0.24 Pg C y^{-1})" (Rabouille et al. 2001: 3615). These results support the conclusion that the proximal coastal oceans are CO_2 sources (0.10 PgC y^{-1}), whereas the distal coastal oceans are CO_2 sinks (0.34 PgC y^{-1}) (Figure 18.2; Gattuso et al. 1998).

Response to Future Forcing

Though small in area, the continental margins are the focal point of land, sea, and atmosphere interactions. They have special significance, not only for biogeochemical cycling and processes, but also increasingly for human habitation. In comparison with the relatively uniform environment of the open oceans, or the rapidly mixing atmosphere, the spatial and temporal heterogeneity of the world's coastal zone is considerable. In addition, human impacts on these relatively small areas are disproportionately large (Pacyna et al. 2000).

Several recent studies show that the continental margins currently function as substantial carbon sinks. Ver et al. (1999a, b) and Mackenzie et al. (2000) estimated a source of 0.2 PgC y^{-1} in the preindustrial era. They argue that the flux has decreased since 1800, a consequence of an ever-increasing nutrient discharge. Recently Mackenzie and coworkers (Rabouille et al. 2001) concluded that the continental margins were net sinks of 0.24 PgC y^{-1} in the preanthropogenic state (Figure 18.2). Assuming that the estimates of Ver et al. (1999a, b) and Mackenzie et al. (2000) were consistently low by 0.44 PgC y^{-1}, the continental margins in 2000 would have been sinks of 0.34 PgC y^{-1}. Though this adjustment may be an oversimplification, it reconciles the air-sea flux of Ver et al. (1999a, b) and Mackenzie et al. (2000) (Figure 18.3) with my result of 0.36 PgC y^{-1} (Figure 18.1). This is a significant fraction (16 percent) of the "global" air-to-sea flux of 2.2 PgC y^{-1} (Takahashi et al. 2002).

The coastal oceans are also strongly influenced by river inputs, which are sensitive to numerous factors, including regional weather and climate, as well as dams and diversions. Rivers are the major conduits for the transfer of water, nutrients, organic material, and particulate matter from land to sea. Inputs of nutrients and organic matter provide critical support for fish breeding in the estuaries. Dams block the downstream transport of particulate matter, an important source of nutrients and food for aquatic biota. A large dam, such as the Nile River's Aswan Dam in Upper Egypt can have a dramatic impact on fish stocks in connected estuaries. The major source of shelf nutrients, however, is onshore advection of subsurface waters (Chen 2000). Decreasing river out-

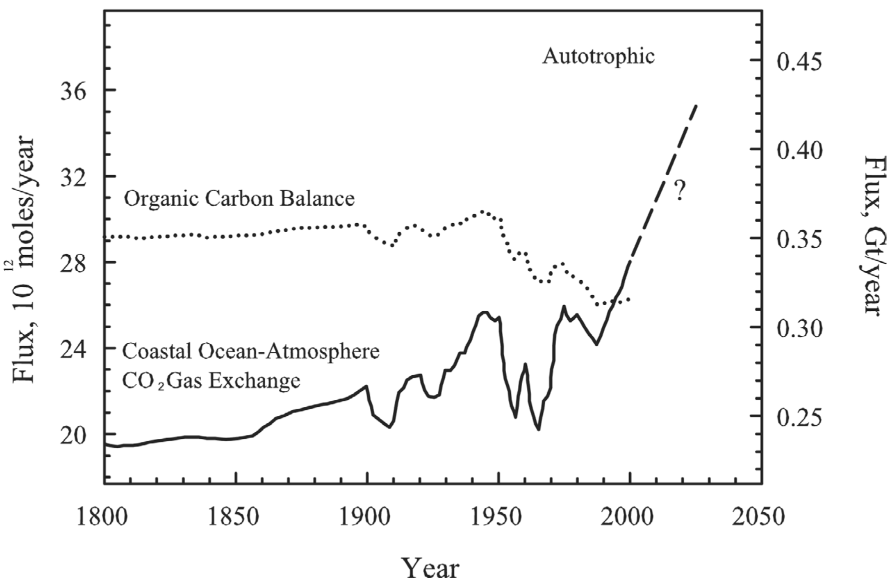

Figure 18.3. Organic carbon balance (dashed line) and net exchange flux of CO2 across the air-seawater interface (solid line) for the coastal margin system, in units of 1012 moles C y-1 and Pg y-1. Positive values indicate the CO_2 flux is directed toward the surface waters (modified from Ver et al. 1999a by adding 36.7 × 1012 mol y-1 or 0.44 Pg y-1 to their results).

flow will reduce the cross-shelf water exchange through a reduced buoyancy effect, and it will also diminish the onshore nutrient supply. Decreased primary production and fish catch on the shelf typically follow dam construction.

Globally, approximately 40 percent of the freshwater and particulate matter entering the oceans is transported by the 10 largest rivers. Buoyant plumes move much of the water and nutrients to the open shelves. Hence, these shelves also experience a diminished biological pump and fish production when damming reduces freshwater outflow. The fraction of riverine particulate carbon that is deposited in the deltas or beaches or converted to the ever-increasing DOC pool is not well known. On the other hand, the coastal oceans may be heterotrophic but nevertheless absorb CO_2.

Conclusions

The first LOICZ report (Kempe 1995) concluded that coastal seas could be net sinks or sources of CO_2 for the atmosphere, with slim prospects for a quick resolution. Now, mass balance calculations, as well as direct pCO_2 measurements, indicate a consistent pattern. Taken together, continental shelves are significant sinks for atmospheric CO_2, absorbing 0.36 PgC a year. This flux is a composite over many estuaries, coastal waters, and intensive upwelling areas, which are typically supersaturated with respect to CO_2, and most open shelf areas, which are probably undersaturated. This "continental shelf pump" is primarily fueled by the cross-shelf transport of nutrients from nutrient-rich subsurface waters offshore. Though they are sinks for CO_2, the shelves release 0.1×10^{12} mol y^{-1} CH_4 and 0.07×10^{12} mol y^{-1} DMS into the atmosphere.

New production supported by the external sources of nutrients represents about 13 percent of primary production. The other 87 percent is respired and recycled on the shelf. Some of the organic material that is not recycled accumulates in the sediments, but most of the detrital organic matter, mainly in its dissolved form, is exported to the slopes and open oceans.

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